STUDIES ON THE MECHANISM OF THE CHUGAEV REACTION

BY

ANTON MUDRAK

B.S., University of Illinois, 1938
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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Introduction

The Chugaev reaction is often used as a means of dehydrating alcohols to olefins in cases where it is desired to avoid rearrangement of the carbon skeleton or the shifting of double bonds.

Previous studies on the mechanism of the reaction (1,2) indicate that it proceeds in a manner different from almost all other elimination reactions. In most of these reactions, elimination of atoms or groups which are *trans* to each other occurs. In the Chugaev reaction, however, removal of a proton appears to be brought about by a frontal attack by one of the sulfur atoms of the xanthate group, resulting in *cis*-elimination.

Because of the unique nature of this mechanism, it seemed desirable to conduct a study which would afford more evidence concerning its validity.

Discussion Of Results

The decomposition of the xanthate of *trans*-2-phenylcyclohexanol gave a product with a refractive index corresponding to a composition of 87.5% 1-phenylcyclohexene and 12.5% 3-phenylcyclohexene. The *cis*-xanthate gave practically pure 3-phenylcyclohexene. These results indicate that the decomposition of xanthates proceeds by *cis*-elimination. A previous study (3) on the same alcohols had shown that acid-dehydration proceeded predominantly by *trans*-elimination.

The *cis* and *trans* isomers of 2-methyl-1-tetralol have been prepared, the former by catalytic reduction of the corresponding ketone with Raney nickel and subsequent purification through the phenylurethan, the latter by sodium reduction of

the ketone.

cis-2-Methyl-1-indanol has been prepared by catalytic reduction of the corresponding ketone with Raney nickel at room temperature and three atmospheres pressure. The *trans* isomer is most readily formed by reduction of the ketone with copper-chromium oxide catalyst at 130° and 2000 p.s.i. pressure. It was shown that the *cis* alcohol isomerizes to the *trans* form under the latter conditions.

The decomposition of the xanthates of *trans*-2-methyl-1-tetralol and *trans*-2-methyl-1-indanol proceeds at a considerably lower temperature than the decomposition of the corresponding *cis* isomers. At 98-100° the decomposition of the *trans*-xanthates was almost complete in twenty minutes whereas the xanthate of *cis*-2-methyl-1-tetralol was stable and the xanthate of *cis*-2-methyl-1-indanol decomposed only to the extent of about 25 percent even after forty-five minutes. It is evident, therefore, that the decomposition proceeds preferentially by *cis*-elimination. However, the fact that the same olefin was formed from the xanthate of both *cis*- and *trans*-2-methyl-1-indanol indicates that some other mechanism of elimination must be available where there is no β-hydrogen atom *cis* to the xanthate group.

A study of the decomposition of the acetates of the above alcohols has shown that the reaction appears to proceed by a mechanism which is analagous to that of the Chugaev reaction (4).

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VITA

The writer was born in Stickney, Illinois, on January 21, 1916. He attended elementary schools in Berwyn, Illinois and the Morton High School of Cicero, Illinois. From September, 1934, to June, 1936, he attended Morton Junior College. In the fall of 1936 he entered the University of Illinois and received the degree of B.S. in Chemistry in June, 1938.

From June, 1938, to July, 1943, he was an analytical chemist in turn with the Carnegie-Illinois Steel Corporation, the Portland Cement Association, both in Chicago, and with the United States Engineers Testing Laboratory at Mariemont, Ohio. In July, 1943, he entered the United States Army and served until March, 1946.

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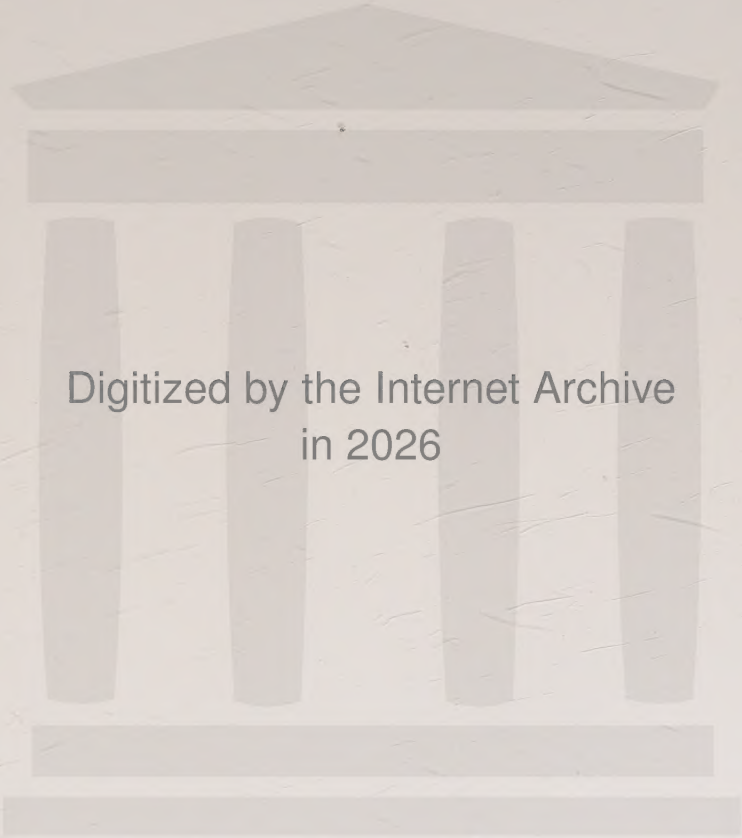
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